Studies on growth, mechanical, spectral and dielectric properties of triglycine sulpho phosphate crystals doped with L-tartaric acid

S.Gracelin Juliana, P.Selvarajan, S.Perumal

***Abstract*— Undoped and L-tartaric acid doped Triglycine Sulpho-phosphate(TGSP) salts were synthesized and single crystals of TGSP were grown by slow evaporation technique. Solubility of the samples for various temperatures in the range 30-50 ^{o}C. It is observed that solubility in water increases with temperature for the samples, showing the positive temperature coefficient. Bulk crystals have been grown from the aqueous solutions of undoped and L-tartaric acid doped Triglycine Sulpho-phosphate. Single crystal XRD studies on the grown crystals reveal the monoclinic crystal structure. Mechanical parameters such as hardness, stiffness constant and yield strength were evaluated. Dielectric studies were performed to ascertain the ferroelectric nature of the samples. SHG and LDT studies reveal the NLO properties of the samples.**

***Index Terms*—Glycine complex, Ferroelectrics, doping, crystal growth, Characterization**

I. INTRODUCTION

Among amino acids, glycine is the simplest amino acid, which has no asymmetric carbon and it has three polymeric crystalline forms viz. α–, β- and γ–glycine. When a-glycine combines with sulphuric acid in the molar ratio 3:1, Triglycine Sulphate (TGS) crystal is formed and it is a suitable material for developing detectors of infrared radiation, environmental analysis monitors, astronomical telescopes, military systems and target faces in vidicons based on the pyroelectric effect. Like TGS crystal, Triglycine Sulpho-Phosphate(TGSP) crystal is also a ferroelectric and pyroelectric material which could be a suitable material for room temperature infrared detection and the other applications. Growth and studies of TGSP crystals was reported by Ravikumar *et al.* [1]. It is obtained by partial substitution of sulphate ions with phosphate ions in TGS crystal and this partial substitution phosphate ions delays microbial contamination during the growth and avoids depolarization with time[2,3]. Aparna Saxena *et al*. reported the various characterization studies on phosphoric acid doped TGS (TGSP) crystals and observed that the dielectric constant of TGSP crystal is low as that of TGS crystal and hence increases the pyroelectric figure of merit [4,5]. Relaxation behaviour of the non-equilibrium domain structure of TGSP crystals was reported[6]. Doping crystals with various kinds of dopants influences the solubility, growth rate, morphology, structural, electrical and other properties of the crystals [7-9]. Metal doped triglycine sulpho-phosphate crystals have been grown and studied by Selvarajan *et al*. [10]. Here, an attempt is made to add an organic material viz. L-tartaric acid as the dopant into TGSP crystals to alter the various properties of the host material.

S.Gracelin Juliana, Department of Physics, Nazareth Margoschis College , Nazareth-628617, Tamilnadu, India.
P.Selvarajan, Department of Physics, Aditanar College of Arts and Science, Tiruchendur-628216, Tamilnadu, India
S.Perumal, Physics Research Centre, S.T. Hindu College, Nagercoil-629003, India.

II. SYNTHESIS AND SOLUBILITY

Saturated aqueous solution of TGSP was prepared using Analar Reagent (AR) grade of glycine, concentrated sulphuric acid and concentrated ortho-phosphoric acid in the molar ratio of 3:0.8:0.2. Synthesized Triglycine Sulpho-Phosphate(TGSP) salt was obtained by heating the saturated solution of TGSP at 50 ^{o}C . Temperature as low as 50 ^{o}C was maintained in order to avoid decomposition of the salt. In accordance with the following chemical reaction, the TGSP salt was synthesized.

$$3(NH_2CH_2COOH) + 0.8\ H_2SO_4 + 0.2\ H_3PO_4 \rightarrow (NH_2CH_2COOH)_3\ H_2SO_4)_{0.8}\ (H_3PO_4)_{0.2}$$

To obtain the doped TGSP salt, L-tartaric acid (1 mole%) was added to aqueous solution of TGSP. The synthesized salt of TGSP and the doped salt were re-crystallized twice and the solubility study was carried out by gravimetrical method[11].The obtained solubility data for L-tartaric acid doped TGSP crystal are 36 g/100 ml at 30 ^{o}C, 39 g/100 ml at 35 ^{o}C, 45 g/100 ml at 40 ^{o}C, 53 g/100 ml at 45 ^{o}C and 57 g/100 ml at 50 ^{o}C and the solubility values for undoped TGSP crystal are observed to be slightly less as compared with those of the doped TGSP sample. Growth of undoped and L-tartaric acid doped TGSP crystals was carried out by solution method with slow evaporation technique. In accordance with the solubility data, the saturated solutions of the re-crystallized salts of undoped and L-tartaric acid doped TGSP were prepared separately using the double distilled water as the solvent. The prepared solutions were constantly stirred well using a magnetic stirrer, filtered using the filter papers. Then, the filtered solutions were kept in the growth vessels separately covered with the porous papers for the growth of undoped and L-tartaric acid doped TGSP crystals. Due to slow evaporation, the single crystals were harvested after a period of 30 days. The grown crystals are shown in the figure 1.

III. RESULTS AND DISCUSSION OF VARIOUS STUDIES

A. XRD studies

The grown undoped and L-tartaric acid doped TGSP single crystals were subjected to single crystal XRD studies

using an ENRAF NONIUS CAD4 diffractometer with MoK$_\alpha$ radiation (λ=0.71073 Å). The obtained XRD data are provided in the table 1. Single crystal XRD analysis indicates that TGSP crystal crystallizes in monoclinic structure with the space group $P2_1$ at room temperature (30 ^oC). The number of molecules per unit cell was found to be 2. The results of XRD data obtained in our work for undoped TGSP crystal are found to be in good agreement with the reported value[12]. It is observed from the results that there is no change of crystal structure when TGSP is doped with L-tartaric acid.

Table 1: Lattice constants of undoped and tartaric acid-doped TGSP crystals

Sample	Lattice constants	V (Å)^3
Undoped TGSP crystal	a= 9.147(1) Å b= 12.723(2) Å , c= 5.786(2) Å α = 90 ^{o}, β= 110.42 (1), γ= 90 ^{o}	631.045(1)
TGSP crystal doped with 1 mole% of tartaric acid	a= 9.204(1), b= 12.597(2), c= 5.595(2) α = 90 ^{o}, β= 107.42 (1), γ= 90 ^{o}	618.94(2)

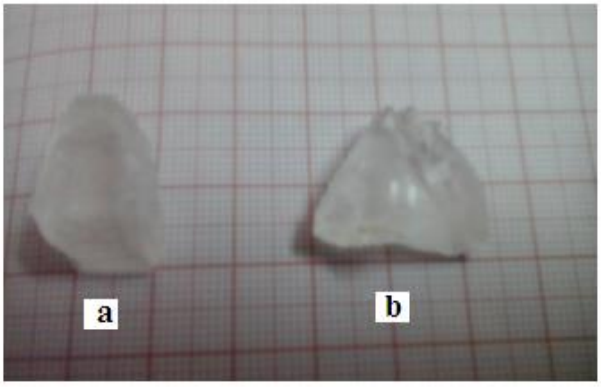

Fig.1: The harvested crystals of (a) undoped and (b) L-tartaric acid doped TGSP crystals

B. *Mechanical properties*

Hardness testing provides information regarding other mechanical properties like tensile strength, yield strength and work hardening coefficient. Transparent crystals free from cracks were selected for microhardness measurements. Microhardness analyses were carried out using Shimadzu Vickers microhardness tester fitted with a diamond indenter attached to an incident light microscope. The well polished crystal was placed on the platform of the Vickers microhardness tester and the loads of different magnitude were applied over a fixed interval of time. Microhardness number was determined using the relation $H_v = 1.8544\ P/d^2$ where P is the applied load and d is the average diagonal indentation. The variation of hardness number with the applied load for the samples is shown in the figure 1. At lower loads, hardness is low and it increases with the load up to 50 g. For loads above 50 g, cracks started developing around the indentation mark. It is due to the release of internal stress generated locally by indentation. It is observed from the results that the hardness increases when TGSP crystal is doped with tartaric acid. This may be due to the incorporation of dopant (tartaric acid) in the interstitials of TGSP crystal. Yield strength of the material can be found out using the relation, yield strength $\sigma_y = (H_v / 3)$ and the stiffness constant (C_{11}) for different loads was calculated the formula $C_{11} = H_v^{7/4}$ where H_v is the microhardness of the material [13]. From results, it is observed that yield strength and stiffness constant of samples show the same behavior as that of hardness number. Due to incorporation of tartaric acid in the host TGSP crystals, the mechanical properties such as hardness, yield strength and stiffness constant are observed to be increased. It seems that the bond strength in the samples increases when L-tartaric acid is added as the dopant and hence the mechanical properties are enhanced.

C. *SHG efficiency*

Second harmonic generation (SHG) is an important second order NLO property and it was measured by Kurtz powder method. The single crystals were powdered and were irradiated by an incident radiation (1064 nm) of pulse width 8 ns from a Q-switched quanta RAY GCR Nd:YAG laser. KDP was used for calibrating the SHG intensity. The output power of the crystal was measured using a power meter and the NLO property of the crystal was confirmed from the estimation of green radiation of the crystal. The obtained values of relative SHG efficiency are 1.33 and 1.75 respectively for undoped and L-tartaric acid doped TGSP crystals.

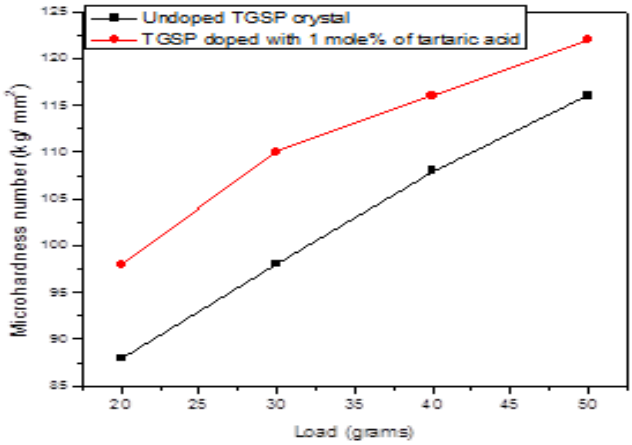

Fig.2: Plots of hardness number versus load for undoped and L-tartaric acid doped TGSP crystals

D. *LDT studies*

Laser damage threshold (LDT) values for the sample crystals were measured using a Nd:YAG laser with the wavelength of 1064 nm. The LDT measurement involves the interaction of high power laser radiation with the matter followed by various physical, chemical, optical, thermal and other processes that are taking place in the material. LDT value is the maximum permissible power that can withstand in a particular crystal and it is determined using the formula $P = E/\tau\pi r^2$ where E is the energy in mJ, τ is the pulse width, r is radius of the spot in mm[14]. The obtained values of LDT for the undoped and L-tartaric acid doped TGSP crystals are 0.86 GW/cm^2 and 0.94 GW/cm^2 respectively.

E. *Dielectric properties*

The dielectric constant and loss factor of the samples were measured using the parallel plate capacitor method at

various temperatures ranging from 30 to 70 °C using an Agilent 4284A LCR meter at different frequencies ranging from 10^2 to 10^6 Hz. The sample cleaved perpendicular to the axis (b-axis) was used. Opposite faces of the sample crystals were coated with good quality silver paste to obtain a good conductive surface layer. The samples were annealed before making observations in the sample holder assembly at 60 °C for about 30 minutes to remove moisture content if present. Since the variation of air capacitance with temperature was found to be negligible, air capacitance was measured only at room temperature. The dielectric constant of the crystal was calculated using the relation

$$\varepsilon_r = C / C_o$$

Where C is the capacitance of the crystal and C_o is the capacitance of the air medium of the same dimension as the crystal. As the crystal area was smaller than the plate area of the cell, parallel capacitance of the portion of the cell not filled with the crystal was taken into account and, consequently, the above equation becomes,

$$\varepsilon_r = \left\{ \frac{C_{crys} - C_{air}\,(1 - A_{crys}/A_{air})}{C_{air}} \right\} \frac{(A_{air})}{(A_{crys})}$$

where C_{crys} is the capacitance with crystal (including air), C_{air} is the capacitance of air, A_{crys} is the area of the crystal touching the electrode and A_{air} is the area of the electrode[15].

Frequency dependence of dielectric constant (ε_r) and dielectric loss ($\tan\delta$) of the undoped and L-tartaric acid doped TGSP crystals at room temperature are shown in the figures 3 and 4. Temperature dependence of the dielectric parameters for the samples at frequency of 1000 Hz are shown in the figures 5 and 6. Dielectric parameters are observed to be decreasing with increase in frequency. Beyond the frequency of 10^4 Hz, the dielectric parameters are found to be practically independent of frequency. Both ε_r and $\tan\delta$ were found to increase when TGSP crystals are doped with L-tartaric acid. The dielectric mechanism of a solid consists of contributions from electronic, ionic, dipolar and space charge polarizations, each dominating in a particular frequency range. It is established that the space charge polarization is very predominant at lower frequencies. The dipolar polarization can be seen in some materials up to 10^{10} Hz. The ionic and electronic polarizations always exist below 10^{13} Hz. From the results, it is observed that the dielectric parameters such as dielectric constant(ε_r) and dielectric loss($\tan\delta$) decrease with increase in frequency. The nature of decrease of ε_r and $\tan\delta$ with frequency suggests that the undoped and L-tartaric acid doped TGSP crystals seem to contain domains of continuously varying relaxation times. The values of dielectric constant and loss are low at higher frequencies because domains of larger relaxation times may not be able to respond to these frequencies. Low value of dielectric loss indicates that the grown crystals are good quality dielectric materials[16,17]. When TGSP crystals are doped with L-tartaric acid, the dielectric constant and loss factor seem to be increasing in the frequency range 10^2-10^6 Hz. The increase in dielectric constant and loss for L-tartaric acid doped TGSP crystals may be due to frittering of domains due to incorporation of impurities in the lattice. This also apparently explains the increase of ε_r and $\tan\delta$ near Curie temperature for the L-tartaric acid doped TGSP sample at 10^3 Hz. The dielectric constant and loss of the samples at the transition temperature (T_c) show finite values and the observed value of Curie temperature for these samples is 51 °C. The values of dielectric constant and loss are found to be more at Curie temperature for the L-tartaric acid doped TGSP crystal compared with the values of pure TGSP crystal. This may be due to presence of more charged impurties in the L-tartaric acid doped TGSP crystal.

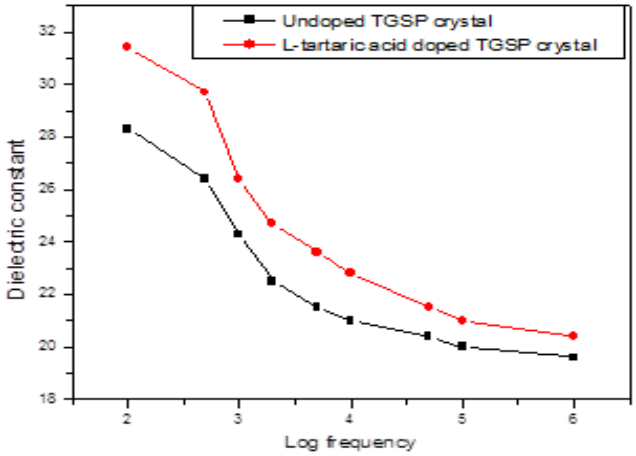

Fig. 3: Variation of dielectric constant with frequency for undoped and L-tartaric acid doped TGSP crystals

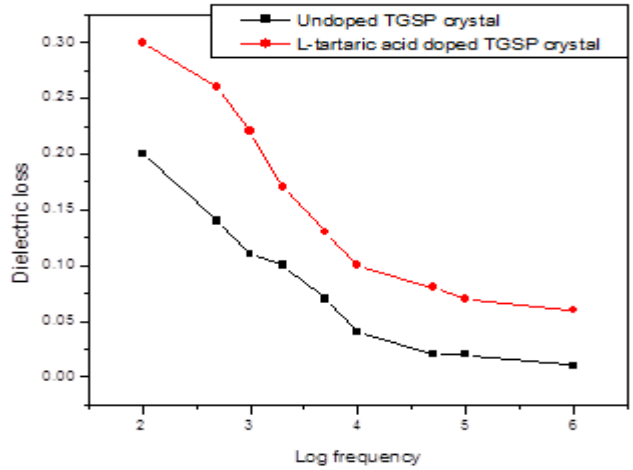

Fig.4: Variation of dielectric loss with frequency for undoped and L- tartaric acid doped TGSP crystals

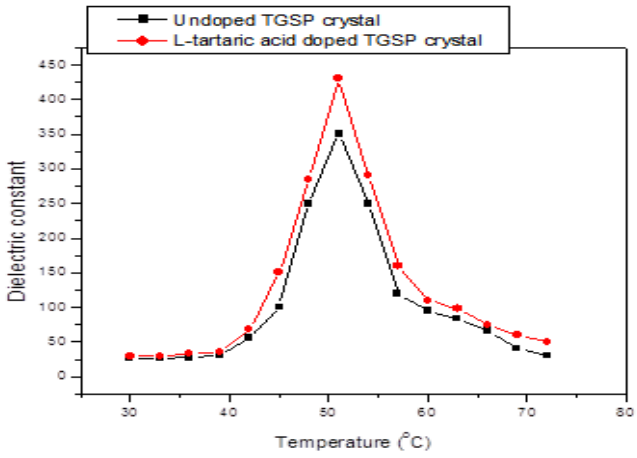

Fig.5: Variation of dielectric constant with temperature for the grown undoped and L-tartaric acid doped TGSP crystals at a frequency of 1000 Hz

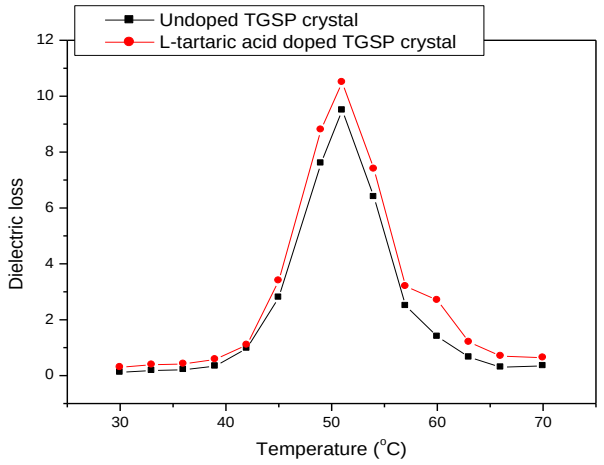

Fig.6:Variation of dielectric loss with temperature for the grown undoped and L-tartaric acid doped TGSP crystals at a frequency of 1000 Hz

IV. CONCLUSIONS

Solution method was adopted to grow pure and L-tartaric acid doped Triglycine Sulpho-phosphate(TGSP) crystals. Solubility of the samples in water was measured at different temperatures and it is found that solubility increases when TGSP sample is doped with L-tartaric acid. XRD studies indicates the monoclinic structure of the crystals. The hardness parameters hardness, stiffness constant and yield strength are found to be enhanced when TGSP samples are added with L-tartaric acid as the dopant. Both the samples are observed to be ferroelectric and the transition temperature is found to be at 51 ^{o}C. SHG and LDT values of the samples were found out and these values seem to be increased when TGSP samples are doped with L-tartaric acid.

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S.Gracelin Juliana is an assistant professor of Physics, doing Ph.D. work. She has an experience in teaching for 15 years and She has published papers in international journals.

Dr.P.Selvarajan has been working as a teacher and researcher for the last 20 years. He is a research guide and published many papers in international journals. His research area is crystal growth and nanotechnology. He is carrying out many research projects.

Dr.S.Perumal is the Principal of S.T.Hindu College, Nagercoil, Tamilnadu. He is a research guide and published many papers in national and international journals. He has carried out major projects and guided many Ph.D. scholars.